Accurate static electric dipole polarizability calculation of +3 charged lanthanide ions

Carine Clavaguéra, Jean-Pierre Dognon

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C. Clavaguéra, J.P. Dognon

Theoretical Chemistry Group

CEA/SACLAY, DSM/DRECAM/SPAM-LFP (CEA-CNRS URA2453)

Bat.522, 91191 GIF SUR YVETTE, France

Abstract

An accurate determination of the heavy element static atomic dipole polarizability is a challenge for theoretical methods. We present in this paper computed values of the dipole polarizability of the lanthanide ions from La^{3+} to Lu^{3+}. The results were obtained by performing fully relativistic and pseudopotential calculations including the treatment of open-shell systems. We have shown that, in order to obtain accurate results, it is essential to take into account scalar relativistic effects, core polarization and flexibility of the basis sets. Finally, we present a database of reference values of dipole polarizability for the Ln^{3+} ions.

1. Introduction

The research concerning the lanthanide elements increases much these last years because of their potential application in the biomedical area. One of the first medical applications is Magnetic Resonance Imaging (MRI). The Gd(III) ion with its seven unpaired electrons is highly paramagnetic and ideal for improving the contrast in MRI. The luminescent properties of the lanthanides are also utilized in medical diagnosis. The ions are generally in hydrated forms, complexed with organic molecules. The observed complexation properties depend on a delicate balance between the different interactions which govern the system and in particular on the polarizing property of the ion (1). So, ion polarizability is one of the fundamental data to understand and model such interactions and must be given with accuracy to be usable in molecular dynamics simulations with polarizable force fields for example (2). Unfortunately, in the case of +3 charged lanthanide ions (Ln^{3+}), there is no experimental polarizability data and very few theoretical data. An accurate determination of the heavy element static atomic polarizabilities is a challenge for theoretical methods. For lanthanides, the more extensive review is given in the Handbook of Atomic Data (3) and is derived from variation-perturbation calculations. Unfortunately, relativistic effects may play an important role and could not be considered as a perturbation (4).

In order to investigate the importance of the relativistic effects on this property, we carried out fully relativistic four-component Dirac-Hartree-Fock (DHF) calculations with response theory and finite-field methods. These calculations can be regarded as reference calculations since they include the scalar relativistic effects and the spin-orbit coupling.

Solutions of the DHF equations involve four-component spinors built in term of large and small components and the application is limited to small size systems. It should be desirable to probe simplified relativistic model with improved computational efficiency in order to

study lanthanide compounds. The Douglas-Kroll (DK) approximation in its scalar one-electron version has been largely used because it is variationaly stable and easy to incorporate in any electronic structure program. Another way is to use pseudopotentials. They are generally obtained from accurate relativistic calculations and provide effective potential for the core electrons. It is within this latter framework that are developed the quasi-relativistic (QR) pseudopotentials (PPs). Only the valence electrons are incorporated in the calculations reducing computational cost. We carried out calculations with these two models and we also investigate the importance of the basis set and the correlation effects in the static dipole polarizability calculation.

2. Theory and computational details

2.1. Polarizability

Static electric dipole polarizabilities were obtained by using the finite electric field perturbation method followed by the numerical differentiation of the field-dependent energies. The static dipole polarizability α_D of an atomic state is defined as (5,6):

$$\alpha_D = -\left(\frac{\partial^2 E(\vec{f})}{\partial f_\mu \partial f_\mu} \right)_{f=0}$$

where $E\left(\vec{f}\right)$ is the total electronic energy as a function of the electric field $\vec{f}$. The calculations were performed with a field strength of 0.005 a.u. This value is small enough to exclude hyperpolarizability effects and large enough to provide significant changes on energy under the effect of the field. We also performed some calculations with a linear response function using the random phase approximation (RPA) as implemented in the DIRAC program for closed-shell systems (7).

2.2. Treatment of the relativistic effects

In order to investigate relativistic effects in dipole polarizability and in the absence of the electron correlation, we have carried out closed-shell and open-shell (average of configurations) calculations in the Dirac-Hartree-Fock (DHF) framework as implemented in the DIRAC program (7).

We use the fully relativistic Dirac Hamiltonian that intrinsically describes both scalar relativistic effects and spin–orbit coupling. For a free particle:

$$\hat{H}_D = c\alpha.\hat{p} + \beta mc^2$$

where $\hat{p} = -i\hbar\nabla$ is the standard definition for the momentum operator, c is the speed of light, m is the rest mass of the electron. α and β could be written in term of the 4x4 Dirac matrices

$$\alpha_x = \begin{pmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{pmatrix} \quad \alpha_y = \begin{pmatrix} 0 & \sigma_y \\ \sigma_y & 0 \end{pmatrix} \quad \alpha_z = \begin{pmatrix} 0 & \sigma_z \\ \sigma_z & 0 \end{pmatrix} \quad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}$$

where σ_x, σ_y, σ_z are the 2x2 Pauli matrices.

It is implemented in the DIRAC code in the framework of the quaternion modified Dirac equation (8). In the present work, the electron-electron interaction is represented by the Coulomb interaction only.

A first level of approximation is to use a spin-free (scalar) relativistic DK Hamiltonian. The DK transformation decouples the large and small components of the DHF wavefunction. We used the DK treatment of scalar relativistic effects as implemented in MOLCAS program package (9).

A second level of approximation is to simplify the electronic problem using pseudopotentials. The relativistic effects are indirectly included through a parametrization of the potential. A fundamental question is the choice of the size of the core and valence subsystems. A useful discussion of this point could be found in reference (4) for lanthanide and actinide elements.

In the present work, we used the quasi-relativistic energy-consistent pseudopotentials of the Stuttgart/Köln group: see the references (10,11) for the large core ones (LC) and the references (12,13) for the small core ones (SC). The large core PPs include the 4f electrons in the core. For these systems with polarizable cores and only few valence electrons (46 + n core electrons with n being the 4f occupation number and 11 valence electrons for lanthanide LC PPs), the HF level should be insufficient for the description of the core-valence interaction if one aims at high accuracy. Wang and Dolg have pointed out that, for lanthanides, both the static (polarization of the core at the HF level) and dynamic (core-valence correlation) polarization of the core need to be taken into account (14). These effects are energetically relatively small but could cause considerable charge redistribution in the valence shells. It should be suitable to consider these effects during the iterative determination of the valence shell wavefunction. Müller and al. (15) have shown that this could be carried out using an effective core polarization potential (CPP) which can be written as:

$$V_{cpp} = -\frac{1}{2}\sum_{c}\alpha_c \vec{f}_c \bullet \vec{f}_c$$

where α_c denotes the dipole polarizability of the core. The electric field f_c which acts on core c due to the charges of the valence electrons i and all others cores *c'* is obtained as:

$$\vec{f}_c = \sum_i \frac{\vec{r}_{ci}}{r_{ci}^3} C(r_{ci},\rho_c) - \sum_{c'\neq c} \frac{\vec{R}_{cc'}}{r_{cc'}^3} Z_{c'} = \vec{f}_c^{\,e} + \vec{f}_{c'}^{\,n}$$

where $\vec{r}_{ci} = \vec{r}_i - \vec{r}_c$ and $\vec{R}_{cc'} = \vec{R}_{c'} - \vec{R}_c$ (atomic units), $C(r_{ci},\rho_c)$ is a cut-off function for the electronic part of $\vec{f}_c$ with an adjustable parameter ρ_c and $Z_{c'}$ is the net charge of the core *c'*. Cut-off functions are necessary in order to avoid electron penetration into the core. The following form has been considered:

$$C(r,\rho_c) = \left[1 - \exp\left(-(r/\rho_c)^2\right)\right]$$

All the calculations have been performed with the MOLPRO program package (16).

2.3. Basis sets

In the evaluation of atomic and molecular electric properties, care needs to be taken of sufficient flexibility of the basis set. This flexibility can be increased by adding polarization functions and by removing the basis set contraction.

For the four-component fully relativistic calculations, we have used the large component family sets developed by Faegri (17):

- for all the lanthanides except La, 23s19p14d9f (d basis set built on the s and f basis set built on the p, with respect to the family set definition),
- for La, 23s19p14d (d built on the s).

We built the basis sets for the lanthanide series according to the same procedure as that implemented by Faegri for La and Lu (18) and adding l+1, l+2, l+3 polarization functions:

- for all the lanthanides except La, 24s20p15d10f3g2h1i (g built from d, h built from f and i built from g),
- for La, 24s20p15d3f2g (f built from p and g built from d).

Small components (ϕ_S) are automatically generated from the large ones (ϕ_L) via the method of kinetic balance approximately with the following relation:

$$\phi_S = \frac{1}{2mc}\sigma.\hat{p}\phi_L.$$

As the result of applying the $\sigma.\hat{p}$ operator, a large component basis of angular moment l generates a small component basis of l+1. So, the small component basis is almost twice larger than the large component one, that involves very large basis sets and high computational cost for all electron fully relativistic calculations.

For the DK calculations, we have used the ANO-type basis sets (19) optimized by the total energy minimization at SCF DK level. We used completely uncontracted basis sets (La: 27s23p15d and Lu: 27s23p15d10f) to be consistent with DHF calculations.

The calculations with LC PPs were performed with the standard associated basis set and also with the initial set augmented by three f-type polarization functions whose exponents were obtained from the d function exponents (the augmented basis sets are available on request to the authors).

3. Calibration studies

3.1. The closed-shell La^{3+} and Lu^{3+}

In Table 1, we present the DHF dipole polarizability data for the La^{3+} and Lu^{3+} ions. In the fully relativistic case, it is observed an identical value from the finite electric field perturbation and RPA methods. It confirms a correct choice for the field strength. On comparing the small and large basis set, it is observed that, if there is no effect on La^{3+} (no f electron), an effect is quite visible on Lu^{3+}. The data obtained with DHF method and Faegri large basis sets will be our reference data in the continuation of the study.

The all electron DK Hamiltonian based calculations with an uncontracted ANO-type basis set (quality close to the Faegri small basis set) give a dipole polarizability value of 1.120 $Å^3$ for La^{3+} and 0.596 $Å^3$ for Lu^{3+}.

In Tables 2 and 3, we present the data for LC PPs with different basis sets and methods. We evaluate the electron correlation contribution to the polarizability with three methods of different complexity. First, the Moller-Plesset second-order perturbation (MP2) method, which is known to give reasonable magnitude of electric properties, may suffer from the presence of near degeneracy. The failure of MP2 method can also be seen from very large values of the electron correlation contribution to the property. The coupled cluster method with single and double excitations corrected perturbatively for the effects of triple excitations (CCSD(T)) is known to perform well in calculation of the electron correlation contribution to electric properties. We have also chosen to evaluate the polarizability with Density Functional

Theory (DFT), B3LYP and PW91 functional, even if a spurious self-interaction contribution and a poor description of the asymptotic behaviour of the electronic distribution can play a part in the polarizability calculation. The polarizability calculated via the DFT should be examined carefully, since the outermost electrons account for most of the polarizability. The basis sets considered in these calculations are smaller than in all electron relativistic calculations. We have investigated the effects of f functions on the computed values of polarizability.

It is observed that at Hartree-Fock (HF) level of approximation and with DFT methods, the *f* orbitals have no effect on the polarizability. As expected, the presence of *f* polarization functions at the correlated level slightly modifies the polarizability value at MP2 and CCSD(T) level. They are needed for a proper polarization of the 5d valence shell.

Another important result is that it is absolutely necessary to use uncontracted basis set, as in our DHF and DK calculations, in order to obtain accurate polarizability data. The flexibility of the basis set is one of the very important points. The effect to uncontract the basis set is more important than that to add polarization functions.

Finally, the best results were obtained with the combination of LC PPs with f-extended uncontracted basis set and CPP. The values thus obtained are very close to those obtained in DHF. It is a very encouraging result in order to study molecular complexes of Ln^{3+}. We also carried out some calculations with SC PPs in order to include explicitly the 4f electrons and more core polarization in the calculation. The HF dipole polarizability values are 1.222 $Å^3$ and 0.598 $Å^3$ respectively (uncontracted standard basis sets). Compared with our reference calculations, these results are worse than those obtained with LC+CPP PPs with for disadvantage a much higher computational cost.

The results also show that the correlation of the valence electrons does not play an important part in the value of polarizability whatever the method used. The CCSD(T) results are not significantly different from the MP2 corrections. The DFT values are too low.

The main conclusion of this first part of the study is that calculation of the atomic dipole polarizability with LC PP associated to CPP is able to reproduce all electron fully relativistic calculations. An additional conclusion is obviously that the spin-orbit coupling does not play an important part in the polarizability as confirmed by the scalar relativistic calculations based on a DK Hamiltonian.

3.2. Role of the spin-orbit coupling on the valence orbital energies

Of course, the spin-orbit coupling could influence the energy of orbitals as shown on Figure 1 for La^{3+} (5s, 5p) and on Figure 2 for Lu^{3+} (5s, 5p, 4f). The energy of the orbitals was obtained from all electron calculations in the frameworks: non-relativistic, DK scalar relativistic, spin-free DHF, fully relativistic DHF and from SC quasi-relativistic PPs calculations. First, we observe the very important role of the relativistic effects on orbital energy values.

In the La^{3+} case, the 5s orbital is highly stabilized (contracted) as a result of the scalar relativistic effects. The 5p orbitals are also stabilized by scalar relativistic effects but to a lesser extent. The spin-orbit coupling splits the 5p shell into $5p_{1/2}$ and $5p_{3/2}$ subshells and destabilizes (expands) the $5p_{3/2}$ shell. We can note that the scalar relativistic effects and spin-orbit interaction tend to cancel for $5p_{3/2}$ shell and to be added for the $5p_{1/2}$ shell.

In the Lu^{3+} case, the same effects are observed for the 5s and 5p shells but, more strongly. The 4f shell is destabilized (expanded) as a result of the scalar relativistic effects. The spin-orbit interaction splits 4f shell into $4f_{5/2}$ and $4f_{7/2}$ subshells with a quite less effect. The effects are all the more important as the element is heavy.

We checked that the field applied in order to calculate the polarizability does not disturb the energy levels of the valence orbitals. In fact, the $4f_{5/2}$ and $4f_{7/2}$ subshells are very slightly splitted, of only 2.10^{-5} a.u what can be considered as negligible.

The spin-free DHF calculations provide degenerated 5p and 4f orbitals at weighted average energies of splitted levels.

3.3. The open-shell case: an example Gd^{3+}

If one wants to study the whole lanthanide series, it is necessary to be able to treat in a satisfactory way the open-shell systems. An evaluation of the effects observed for the closed-shell systems is necessary. So, we decide to perform our open-shell calibration study on the Gd^{3+} ion, which is in the middle of the lanthanide series with seven unpaired f electrons. We have adopted an average configuration procedure to solve the relativistic open-shell SCF equations (20), (21). In the Gd^{3+} case, the seven f electrons were distributed over the full f spin-orbital space with a fractional occupation number (0.5 electron in this case). The DHF polarizability values are 0.819 $Å^3$ and 0.835 $Å^3$ with small and large basis sets respectively. The basis set effect is larger than for the closed-shell cases what is not very surprising in a seven electrons open-shell system. The value obtained with the large basis set will be the reference for the Gd^{3+} ion.

Table 4 supplies the LC PP data to evaluate method, basis set and CPP effects. The main conclusions are the same ones as for the La^{3+} and Lu^{3+} closed-shell systems. We confirm the importance of a wide flexibility of the basis set, i.e. need for using polarization functions and uncontracted basis sets, to obtain accurate polarizability data for f elements. Core polarization effects are large in this system as for the Lu^{3+} case due to the presence of the f shell in the PP core.

4. Lanthanide series

The results from DHF, LC PPs with and without CPP, with and without electron correlation (from CCSD(T)) calculations are summarized in Table 6 and Figure 3.

As already pointed out by Dolg (4), the main problem for the generation of the CPP is that we do not have any experimental references to determine the parameters of the potential (dipole polarizability of the core and cut-off value). As the calculations are not too sensitive to the value of the CPP parameters, the Dolg α_c values (4) for La and Lu were used to interpolate those of the other lanthanide elements. The resulting parameters are given in Table 5. The value of the cut-off was taken to 0.5592 (4).

All the calculations were performed with the uncontracted standard basis set augmented with three f functions.

The reference values are those that we obtained with large basis set DHF calculations with average configurations for open-shell systems. This additional difficulty involves higher computational cost. We can note, in this case, a slight effect of the basis set size on the polarizability value for the medium of the series (Eu^{3+}, Gd^{3+}). We encountered SCF convergence problems in DHF calculations for Ce^{3+} and Pr^{3+}. The data given in these two cases are interpolated values starting from a polynomial of degree 3 and the data of the other lanthanides. Our DHF values obtained are very different from those given in the Handbook of Atomic Data (3). The variation-perturbation method must lie above our reference values (6).

In the PP calculations, we can see that the addition of the CPP improves the calculated dipole polarizability values in all cases especially for the second half of the series (cf. Figure 3). We can note that the HF LC + CPP results are not so different than the correlated ones and very close to the all electron DHF results confirming that the scalar relativistic effects are the dominating effects in the dipole polarizability property. This can be seen on Figure 3 in which one observes a regular decrease of the dipole polarizability according to the atomic number.

We note that the slight difference observed for the middle of the series between DHF and HF LC + CPP could be assigned to the open shell treatment with average of configurations for highly multireference character systems.

5. Conclusions

We propose in this work a reference database for the atomic dipole polarizability of Ln^{3+} ions obtained from DHF calculations, i.e. by taking into account the scalar relativistic effects and the spin-orbit coupling. The flexibility of the basis set plays a very important part in the value of dipole polarizability. It is essential to use uncontracted basis set and to include polarization functions. It is also fundamental to take into account the scalar relativistic effects to have accurate values of Ln^{3+} dipole polarizability. Under these conditions, we showed that quasi-relativistic PPs associate with CPPs are able to give results close to all electron fully relativistic calculations including in the case of open-shell systems and this at quite lower computational cost. Dipole polarizability is a property that depends as well on the electronic structure of the valence shells as of the core polarization process.

In a future work, we will apply and extend this methodology to elements for which the relativistic effects are even more important, for example the actinide ions.

Acknowledgements

We thank Michael Dolg for very fruitful discussions concerning relativistic effects and for supplying information about CPP. We thank Knut Faegri for his assistance to use his four-component basis sets.

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Table 1: DHF atomic dipole polarizabilities for La^{3+} and Lu^{3+} (in $Å^3$)

Ln^{3+}	Finite field		RPA	
	Small basis set	Large basis set	Small basis set	Large basis set
La^{3+}	1.134	1.136	1.134	1.136
Lu^{3+}	0.606	0.612	0.606	0.612

Table 2: La^{3+} atomic dipole polarizability data (in $Å^3$)

Method	*Basis set*	*LC No f*	*LC With f*	*LC No f + CPP*	*LC With f + CPP*
HF	Cont.	1.120	1.120	1.121	1.121
	Uncont.	1.130	1.131	1.131	1.131
MP2	Cont.	1.102	1.130	1.108	1.125
	Uncont.	1.090	1.130	1.118	1.133
CCSD(T)	Cont.	1.104	1.130	1.109	1.125
	Uncont.	1.114	1.131	1.121	1.134
B3LYP	Cont.	1.123	1.123	1.116	1.116
	Uncont.	1.130	1.130	1.124	1.124
PW91	Cont.	1.124	1.124	1.115	1.115
	Uncont.	1.131	1.131	1.122	1.122

"Cont." and "Uncont." for contracted and uncontracted basis set, "LC" for large core PP, "CPP" for core polarization potential.

Table 3: Lu^{3+} atomic dipole polarizability data (in $Å^3$)

Method	*Basis set*	*LC No f*	*LC With f*	*LC No f + CPP*	*LC With f + CPP*
HF	Cont.	0.540	0.540	0.604	0.604
	Uncont.	0.547	0.547	0.617	0.617
MP2	Cont.	0.535	0.542	0.607	0.608
	Uncont.	0.539	0.548	0.620	0.623
CCSD(T)	Cont.	0.536	0.543	0.608	0.608
	Uncont.	0.541	0.549	0.621	0.623
B3LYP	Cont.	0.549	0.549	0.595	0.595
	Uncont.	0.553	0.553	0.604	0.604
PW91	Cont.	0.551	0.551	0.592	0.592
	Uncont.	0.555	0.555	0.601	0.601

"Cont." and "Uncont." for contracted and uncontracted basis set, "LC" for large core PP, "CPP" for core polarization potential.

Table 4: Gd^{3+} atomic dipole polarizability data (in $Å^3$)

Method	*Basis set*	*LC No f*	*LC With f*	*LC No f + CPP*	*LC With f + CPP*
HF	Cont.	0.758	0.758	0.776	0.776
	Uncont.	0.765	0.765	0.786	0.786
MP2	Cont.	0.747	0.764	0.775	0.783
	Uncont.	0.751	0.764	0.786	0.789
CCSD(T)	Cont.	0.748	0.764	0.775	0.783
	Uncont.	0.755	0.765	0.786	0.790
B3LYP	Cont.	0.763	0.763	0.766	0.766
	Uncont.	0.766	0.766	0.773	0.773
PW91	Cont.	0.765	0.765	0.764	0.764
	Uncont.	0.765	0.765	0.770	0.770

"Cont." and "Uncont." for contracted and uncontracted basis set, "LC" for large core PP, "CPP" for core polarization potential.

Table 5: α_c CPP parameters for the Ln^{3+} series (a.u.)

La	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**
0.4777	0.5851	0.6925	0.7999	1.0147	1.1221	1.2295
Tb	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
1.3369	1.4442	1.5516	1.6590	1.7664	1.8738	1.9812

Table 6: Ln^{3+} series dipole polarizability: DHF values with small and large basis sets, HF and CCSD(T) values with LC PP with their associated uncontracted augmented basis set with and without CPP. Values in italics are interpolated values (see the text).

Ln	At. number	DHF		LC		LC+CPP		Reference (3)
		Small basis set	Large basis set	HF	CCSD(T)	HF	CCSD(T)	
La^{3+}	57	1.134	1.136	1.130	1.131	1.131	1.134	1.410
Ce^{3+}	58	*1.086*	*1.090*	1.059	1.060	1.062	1.065	1.350
Pr^{3+}	59	*1.039*	*1.045*	0.999	1.000	1.004	1.007	1.290
Nd^{3+}	60	0.997	1.001	0.945	0.945	0.952	0.955	1.230
Sm^{3+}	62	0.902	0.906	0.846	0.846	0.859	0.862	1.170
Eu^{3+}	63	0.859	0.875	0.802	0.802	0.820	0.823	1.110
Gd^{3+}	64	0.819	0.835	0.765	0.765	0.786	0.790	1.060
Tb^{3+}	65	0.782	0.786	0.726	0.727	0.753	0.757	1.010
Dy^{3+}	66	0.747	0.752	0.691	0.691	0.724	0.728	0.970
Ho^{3+}	67	0.715	0.720	0.658	0.659	0.698	0.702	0.940
Er^{3+}	68	0.685	0.690	0.628	0.628	0.675	0.678	0.900
Tm^{3+}	69	0.657	0.662	0.599	0.600	0.654	0.658	0.860
Yb^{3+}	70	0.631	0.636	0.572	0.573	0.636	0.640	0.800
Lu^{3+}	71	0.606	0.612	0.547	0.549	0.617	0.623	0.770

Figure captions

Figure 1: valence orbital energies for La^{3+} from various calculation levels

Figure 2: valence orbital energies for La^{3+} from various calculation levels

Figure 3: variation of the dipole polarizability along the lanthanide series as the atomic number (data from Table 6)

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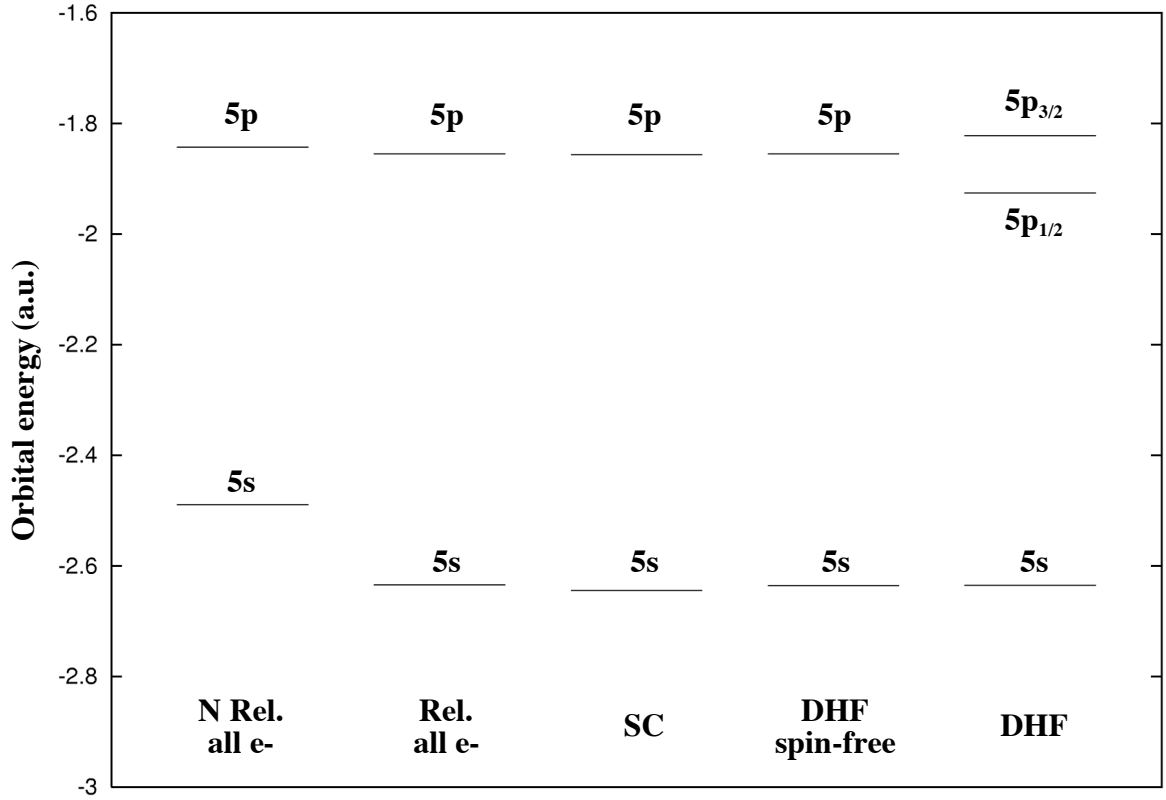

" N Rel. all e-" for non-relativistic all electron, "Rel. all e-" for DK all electron, "SC" for small core PP

Figure 2: valence orbital energies for La^{3+} from various calculation levels

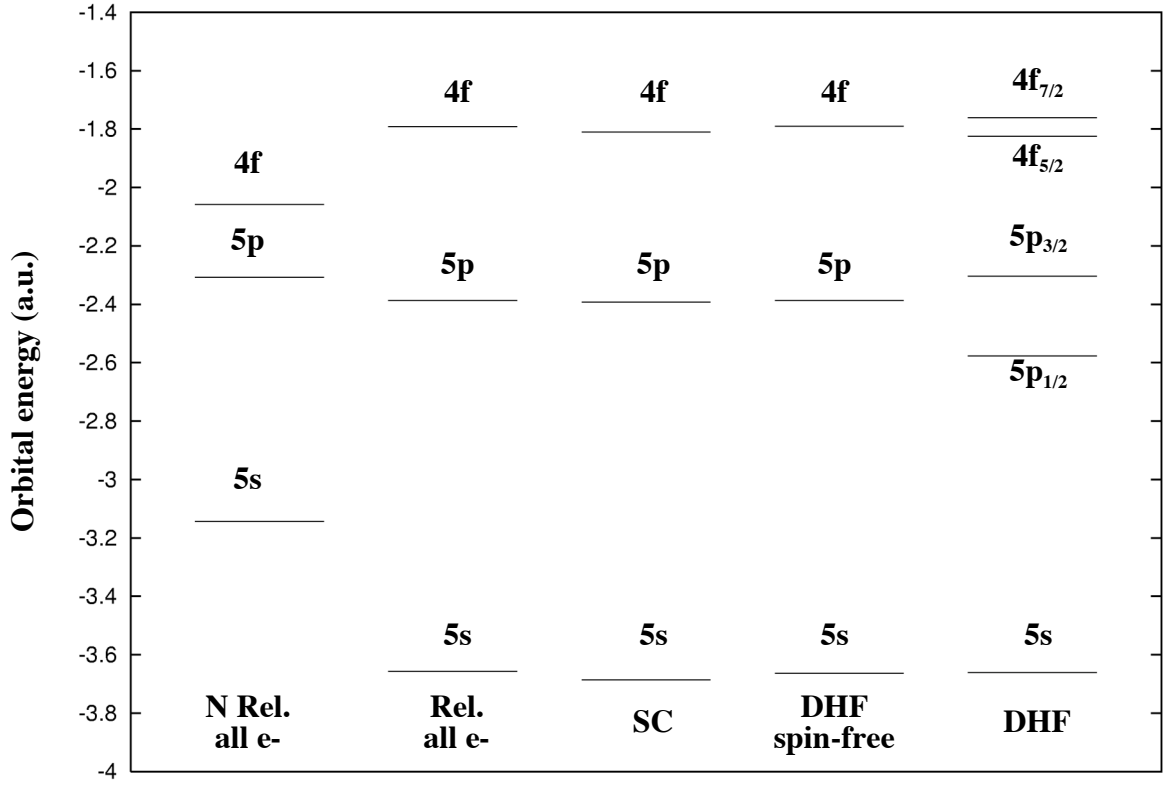

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Figure 3: variation of the dipole polarizability along the lanthanide series as the atomic number (data from Table 6)